Metallation of Diazines. III. New Synthesis of Analogues of Trimethoprim and of Bacimethrin

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Received June 11, 1990

4-Chloro-2,6-dimethoxypyrimidine was lithiated by lithium 2,2,6,6-tetramethylpiperidide. The resulting lithio derivative was submitted to reaction with carbonyl derivatives, iodine and trimethyltin chloride. Synthesis of analogues of trimethoprim and of bacimetrin are reported.

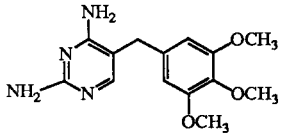
J. Heterocyclic Chem., **28**, 283 (1991).

Introduction.

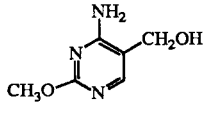
A pyrimidine skeleton is commonly found in pharmaceutical drugs, fungicides and herbicides. Reported preparations of such pyrimidine compounds has been based on classical condensation reactions which involve the pyrimidine ring construction. As a continuation of our studies of direct metallation of diazines [1,2] we have turned our attention to synthesis of some new pyrimidine derivatives by lithiation.

In a previous paper [2] we reported the direct metallation of 2,4-dichloropyrimidine and described an original problem of regioselectivity.

We report here the synthesis of analogues of trimethoprim **1** and bacimethrin **2**, which are well known for their antibacterial activity, by lithiation of 4-chloro-2,6-dimethoxypyrimidine.



1



2

In the pyrimidine system there are few reports dealing with *ortho*-directed lithiation [3-6] of pyrimidine bearing an *ortho* activating group on a carbon atom.

First we wish to report the metallation of 4-chloro-2,6-dimethoxypyrimidine **3**.

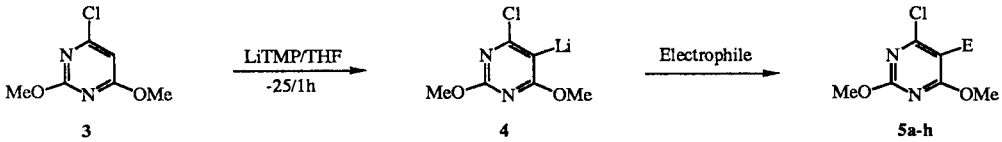
Treatment of **3** in tetrahydrofuran (THF) with 1.1 equivalents of lithium 2,2,6,6-tetramethylpiperidide (LiTMP) as the metallating agent at −25° for 1 hour leads to the lithio derivative **4** which was submitted to the reaction of various electrophiles (Scheme I).

The accumulation of lithio derivative **4** in the reaction medium before the addition of an electrophile can be determined by quenching with methanol-*O*-d and analysing the resultant mixture by ^{1}H nmr spectroscopy. After 1 hour at −25° an excellent accumulation rate (~90%) is observed. The reactivity of lithio derivative **4** with various electrophiles such as acetaldehyde, benzaldehyde, *O*-anisaldehyde, 3,4,5-trimethoxybenzaldehyde, ethyl formate, iodine and trimethyltin chloride was investigated and compounds **5a-h** are obtained with good yield.

In the case of ethyl formate as an electrophile, addition of ethyl formate at −25° led to the secondary alcohol **6** (Scheme II), the expected aldehyde was obtained when the addition temperature of electrophile was lower (−70°).

The secondary alcohols **5** and **6** are readily oxidized with manganese(IV) oxide to give ketones **7** and **8** in good yields (Scheme III).

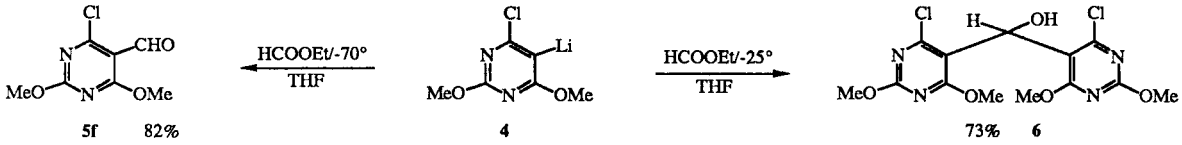
Scheme I



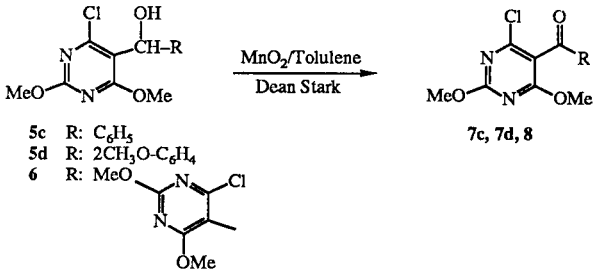
3 **4** **5a-h**

5a	*E*:D	90%	5e	*E*:CH(OH)-(2,4,5-trimethoxyphenyl)	65%
5b	*E*:CH(OH)-CH_3	88%	5f	*E*:CHO	82%
5c	*E*:CH(OH)-Ph	87%	5g	*E*:I	86%
5d	*E*:CH(OH)-(2-methoxyphenyl)	86%	5h	*E*:Sn(Me)$_3$	62%

Scheme II



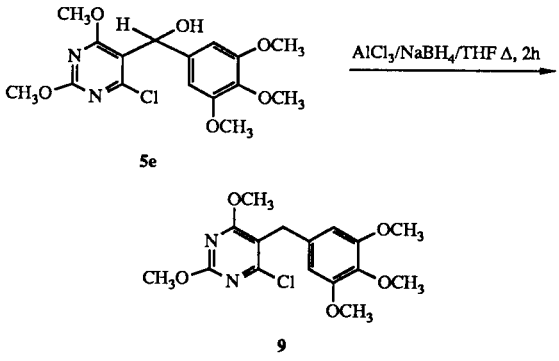
Scheme III



Interposition of a methylene group between the phenyl ring and the diamino-2,4-pyrimidines leads to the benzyl-diaminopyrimidines, a class of compounds known for their antibacterial activity [7-10]. The best known of them is the trimethoprim **1**.

Hydrogenolysis of compound **5e** to 3,4,5-trimethoxy-phenyl-2-chloro-4,6-dimethoxypyrimidylmethane **9** (Scheme IV) was performed by sodium borohydride and anhydrous aluminium(III) chloride in tetrahydrofuran [11]. The methylenic hydrocarbon **9** was obtained in a moderate yield (57%). A further catalytic reduction of **9** with palladium on carbon used as catalyst gives **10** an analogue of trimethoprim (Scheme V).

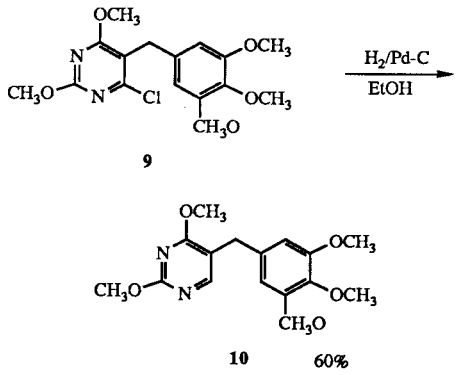
Scheme IV



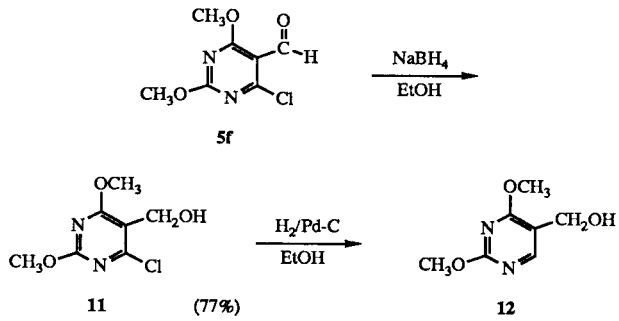
An analogue of bacimethrin **2** is obtained by reduction of 4-chloro-5-formyl-2,6-dimethoxypyrimidine **5f** (Scheme VI).

Reduction of **5f** by sodium borohydride in ethanol gives the primary alcohol **11** with a good yield (77%); a further catalytic reduction removes the chlorine atom and **12** an analogue of bacimethrin is obtained.

Scheme V



Scheme VI



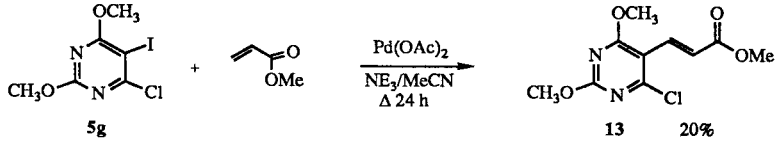
The palladium catalyzed cross coupling reaction of aryl halides with olefins has found wide application in organic synthesis [12]. Nevertheless there are to our knowledgment few reports dealing with cross-coupling reaction between iodopyrimidines and alkenes [13-15].

We wish to report the palladium catalyzed coupling reaction of 4-chloro-2,6-dimethoxy-5 iodopyrimidine **5g** with methyl acrylate.

Coupling reaction of **5g** with methyl acrylate was performed in acetonitrile with triethylamine, 3 equivalents of methyl acrylate in presence of a catalytic amount of palladium diacetate triphenylphosphine complex. The mixture reaction was heated under reflux for 24 hours (Scheme VII).

Under these experimental conditions compound **5g** afforded 4-chloro-2,6-dimethoxy-5-(*E*)-(methoxycarbonylethenyl)pyrimidine **13** which has a configuration *E*. The low yield observed (20%) for the coupling product can be explained either by a steric hindrance or by formation of reduction compounds. The occurence of such saturated com-

Scheme VII



pounds were noticed by Wada *et al* [15], when coupling 5-iodopyrimidines and vinyl ketones. However, we could not identify or isolate reduction compounds.

Thus, we demonstrated that *ortho*-directed lithiation in the pyrimidine system afforded various substituted pyrimidines. Ready access to *O*-functionalyzed 5-acyl or 5-formylpyrimidines is of general interest to synthesize derivatives of biological interest and further investigations in this area are currently in progress.

EXPERIMENTAL

Melting points were determined on a Kofler hot stage and are uncorrected. The ^{1}H nmr spectra were recorded in deuteriochloroform with tetramethylsilane as the internal standard or in deuterated dimethyl sulfoxide with hexamethyldisiloxane as the internal standard on a Varian EM 360 L instrument. Microanalyses were performed on a Carlo Erba CHNOS 1106 apparatus. The ir spectra were obtained as potassium bromide pellets with a Perkin Elmer R12 spectrophotometer.

Tetrahydrofuran was distilled from benzophenone sodium and used immediately. Water content of the solvent was estimated by the modified Karl-Fischer method (THF less than 50 ppm water).

Metallations were performed under an argon atmosphere whose water content was regularly checked. Reagents were handled with syringes through septa.

General Procedure for Metallation.

A solution of butyllithium (1.6 *M* in hexane, 3 ml, 4.8 mmoles) was added to cold (−30°), stirred anhydrous tetrahydrofuran (40 ml) under an atmosphere of dry argon. The mixture was warmed to 0° and 2,2,6,6-tetramethylpiperidine (0.91 ml, 5.4 mmoles) was added, the solution was kept at 0° for 30 minutes, it was then cooled to −25°. A solution of 0.65 g of 4-chloro-2,6-dimethoxypyrimidine (4.0 mmoles) in 5 ml of tetrahydrofuran was added and the mixture was stirred for 1.5 hours at −25°. The electrophile was added and stirring was continued for 1 hour at −25°. Hydrolysis was then carried out at −25° using a mixture of 35% aqueous hydrochloric acid (2 ml), ethanol (2 ml) and tetrahydrofuran (8 ml). The solution was gently warmed to room temperature, made slightly basic with a saturated sodium bicarbonate solution (10 ml) and evaporated under vacuum nearly to dryness. The residue was extracted with dichloromethane (3 x 50 ml). The organic extract was dried (magnesium sulphate) and evaporated. The crude product was purified by column chromatography on silica gel or by sublimation.

4-Chloro-5-deuterio-2,6-dimethoxypyrimidine **5a**.

Metallation of **4** (0.65 g, 4.0 mmoles) according to the general procedure and reaction with 1 ml of mixture perdeuteriomethanol-deuterium chloride 1:1 gave 0.62 g (90%) of **5a**. The crude product was purified by sublimation, mp 75°; ^{1}H nmr (deuteriochloroform): δ 3.97 (s, 3H, OCH_3), 4.00 (s, 3H, OCH_3) ppm.

(4-Chloro-2,6-dimethoxy-5-pyrimidinyl)ethanol **5b**.

Metallation of **4** (0.65 g, 4.0 mmoles) according to the general procedure and reaction with acetaldehyde (2 ml, 36 mmoles) gave after purification by column chromatography on silica gel with a mixture of dichloromethane-ethyl acetate 9:1 as an eluent 77 mg (88%) of **5b**, mp 78°; ^{1}H nmr (deuteriochloroform): δ 1.49 (d, 3H, CH_3, J = 7 Hz), 2.92 (d, 1H, OH, J = 9.3 Hz), 3.96 (s, 3H, OCH_3), 4.05 (s, 3H, OCH_3), 5.16 (m, 1H, CH) ppm.

Anal. Calcd. for $C_8H_{11}ClN_2O_3$: C, 43.93; N, 12.81; H, 5.03. Found: C, 43.5; N, 12.6 H, 5.0.

(4-Chloro-2,6-dimethoxy-5-pyrimidinyl)phenylmethanol **5c**.

Metallation of **4** (0.65 g, 4.0 mmoles) according to the general procedure and reaction with benzaldehyde (0.6 ml, 5.65 mmoles) gave after purification by column chromatography on silica gel with a mixture of dichloromethane-ethyl acetate 9:1 as an eluent 976 mg (87%) of **5c**, mp 89°; ^{1}H nmr (deuteriochloroform): δ 3.40 (s, 1H, OH), 4.03 (s, 3H, OCH_3), 4.08 (s, 3H, OCH_3), 6.22 (s, 1H, CH), 7.36 (s, 5H, phenyl) ppm; ir (potassium bromide); ν 3400, 1590, 1550, 1500 cm^{-1}.

Anal. Calcd. for $C_{13}H_{13}ClN_2O_3$: C, 55.61; N, 9.98; H, 4.61. Found: C, 56.0; N, 9.6; H, 4.8.

(4-Chloro-2,6-dimethoxy-5-pyrimidinyl)-2-methoxyphenylmethanol **5d**.

Metallation of **4** (0.65 g, 4.0 mmoles) according to the general procedure and reaction with 2-methoxybenzaldehyde (0.45 ml, 3.8 mmoles) gave after purification by column chromatography on silica gel with a mixture of dichloromethane-ethyl acetate 9:1 as an eluent 1.07 g (86%) of **5d**, mp 108°; ^{1}H nmr (deuteriochloroform): δ 3.50 (s, 1H, OH), 3.76 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 6.98 (s, 1H, CH), 6.7-7.6 (m, 4H, phenyl) ppm; ir (potassium bromide): ν 3400, 1590, 1550, 1490 cm^{-1}.

Anal. Calcd. for $C_{14}H_{15}ClN_2O_4$: C, 54.11; N, 9.02; H, 5.04. Found: C, 54.2; N, 8.7; H, 4.8.

(4-Chloro-2,6-dimethoxy-5-pyrimidinyl)-3,4,5-trimethoxyphenylmethanol **5e**.

Metallation of **4** (0.65 g, 4.0 mmoles) according to the general procedure and reaction with 3,4,5-trimethoxybenzaldehyde (0.63 g, 3.27 mmoles) gave after purification by column chromatography on silica gel with dichloromethane as an eluent 965 mg (65%) of **5e**, mp 136°; ^{1}H nmr (deuteriochloroform): δ 3.43 (d, 1H, OH, J = 10.6 Hz), 3.85 (s, 9H, OCH_3), 4.00 (s, 3H, OCH_3), 4.02 (s, 3H, OCH_3), 6.13 (d, 1H, CH), 6.58 (s, 2H, phenyl) ppm; ir (potassium bromide): ν 3440, 1590, 1550, 1500 cm^{-1}.

Anal. Calcd. for $C_{16}H_{19}ClN_2O_6$: C, 51.82; N, 7.56; H, 5.13. Found: C, 51.6; N, 7.1; H, 5.4

4-Chloro-5-formyl-2,6-dimethoxypyrimidine **5f**.

A solution of butyllithium (1.6 *M* in hexane, 3 ml, 4.8 mmoles) was added to cold (−30°), stirred, anhydrous tetrahydrofuran (40 ml) under an atmosphere of dry argon. The mixture was warmed to 0° for 30 minutes, it was cooled to −25°. A solution of 0.65 g of 4-chloro-2,6-dimethoxypyrimidine (4.0 mmoles) in 5 ml of tetrahydrofuran was added and the mixture was stirred for 1.5 hour at −25°, the mixture was then cooled to −70°, the ethyl formate (0.31 ml, 3.8 mmoles) was added, stirring was continued for 1 hour at −70°. Hydrolysis was then carried out at −70° using a mixture of 35% aqueous hydrochloric acid (2 ml), ethanol (2 ml) and tetrahydrofuran (8 ml). The solution was gently warmed to room temperature, made slightly basic with a saturated sodium hydrogenocarbonate solution (10 ml) and evaporated under vacuum nearly to dryness. The residue was extracted with dichloromethane (3 x 50 ml). The organic extract was dried (magnesium sulfate) and evaporated. The crude product was purified by column chromatography on silica gel with a mixture of dichloromethane-ethyl acetate 9:1 as an eluent, to give 665 mg (86%) of **5f**, mp 97; ^{1}H nmr (deuteriochloroform): δ 4.00 (s, 3H, OCH_3), 4.05 (s, 3H, OCH_3), 8.21 (s, 1H, CHO) ppm; ir (potassium bromide): ν 2950, 1720, 1580, 1530, 1500 cm^{-1}.

Anal. Calcd. for $C_7H_7ClN_2O_3$: C, 41.46; N, 13.82; H, 3.45. Found: C, 41.3; N, 13.6; H, 3.4.

6-Chloro-5-iodo-2,4-dimethoxypyrimidine **5g**.

Metallation of **4** (0.65 g, 4.0 mmoles) according to the general procedure and reaction with a solution of 1.1 g (3.8 mmoles) of iodine in 5 ml of tetrahydrofuran gave after sublimation (80°, 0.1 Torr) 1.03 g (86%) of **5g**, mp 127°; ^{1}H nmr (deuteriochloroform): δ 4.05 (s, 3H, OCH_3), 4.10 (s, 3H, OCH_3) ppm; ir (potassium bromide): ν 3000, 1550, 1480 cm^{-1}.

Anal. Calcd. for $C_6H_6ClN_2O_2$: C, 23.95; N, 9.31; H, 2.00. Found: C, 24.0; N, 9.2; H, 1.9.

6-Chloro-2,4-dimethoxy-5-trimethylstannylpyrimidine **5h**.

Metallation of **4** (0.65 g, 4.0 mmoles) according to the general procedure and reaction with a solution of 0.8 g (4 mmoles) of trimethyltin chloride in 5 ml of tetrahydrofuran gave after purification by column chromatography on silica gel with dichloromethane, as an eluent 835 mg (62%) of **5h**, mp 57°; ^{1}H nmr (deuteriochloroform): δ 0.42 (s, 9H, CH_3), 3.97 (s, 3H, OCH_3), 4.02 (s, 3H, OCH_3) ppm; ir (potassium bromide): ν 2990, 1560, 1540, 1480 cm^{-1}.

Anal. Calcd. for $C_9H_{15}ClN_2O_2Sn$: C, 32.09; N, 8.32; H, 4.46. Found: C, 32.0; N, 8.1; H, 4.3.

Bis(4-chloro-2,6-dimethoxy-5-pyrimidinyl)methanol **6**.

Metallation of **4** (0.65 g, 4.0 mmoles) according to the general procedure and reaction with 0.31 ml (3.8 mmoles) of ethyl formate gave after purification by column chromatography on silica gel with a mixture of dichloromethane-ethyl acetate 9:1 as an eluent 1.05 g (73%) of **6**, mp 122°; ^{1}H nmr (deuteriochloroform): δ 4.03 (s, 12H, OCH_3); 4.43 (d, 1H, OH), 6.33 (d, 1H, CH, J = 11 Hz) ppm; ir (potassium bromide): ν 3540, 3420, 3000, 1585, 1500 cm^{-1}.

Anal. Calcd. for $C_{13}H_{14}Cl_2N_4O_5$: C, 41.38; N, 14.85; H, 3.71. Found: C, 41.3; N, 14.6; H, 3.6.

General Procedure for Oxidation of Alcohols in Ketones.

In a flask equipped with a Dean-Stark trap, a mixture of the secondary alcohol (1.0 mmole), anhydrous toluene (50 ml) and freshly prepared manganese(IV) oxide (2 g, 23 mmoles) was heated to boiling for 1 hour. The mixture was then filtered and the precipitate was extracted with tetrahydrofuran (3 x 20 ml). The combined filtrate and extracts were dried (magnesium sulfate) and evaporated. The crude product was purified by column chromatography on silica gel by sublimation.

(4-Chloro-2,6-dimethoxy-5-pyrimidinyl)benzophenone **7c**.

Oxidation of **5c** according to the general procedure gave after purification by sublimation (130°, 0.1 Torr) 239 mg (86%) of **7c**, mp 112°; ^{1}H nmr (deuteriochloroform): δ 3.94 (s, 3H, OCH_3), 4.07 (s, 3H, OCH_3), 7.44-7.9 (m, 5H, phenyl) ppm; ir (potassium bromide): ν 3060, 3000, 1660, 1600 cm^{-1}.

Anal. Calcd. for $C_{13}H_{11}ClN_2O_3$: C, 56.01; N, 10.05; H, 3.95. Found: C, 55.9; N, 9.7; H, 3.8.

(4-Chloro-2,6-dimethoxy-5-pyrimidinyl) 2-Methoxyphenyl Ketone **7d**.

Oxidation of **5d** according to the general procedure gave after purification by column chromatography on silica gel with a mixture dichloromethane, ethyl acetate 9:1 as an eluent 230 mg (75%) of **7d**, mp 110°; ^{1}H nmr (deuteriochloroform): δ 3.68 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 4.06 (s, 3H, OCH_3); 6.8-8.0 (m, 4H, phenyl) ppm; ir (potassium bromide): ν 3000, 2940, 1660, 1600 cm^{-1}.

Anal. Calcd. for $C_{14}H_{13}ClN_2O_4$: C, 54.46; N, 9.08; H, 4.21. Found: C, 54.5; N, 9.0; H, 4.0.

Bis(4-chloro-2,6-dimethoxy-5-pyrimidinyl) Ketone **8**.

Oxidation of **6** according to the general procedure gave after purification by sublimation (140°, 0.1 Torr) 116 mg (31%) of **8**, mp 150°; ^{1}H nmr (deuteriochloroform): δ 3.97 (s, 6H, OCH_3), 4.07 (s, 6H, OCH_3); ir (potassium bromide): ν 1690, 1570, 1540 cm^{-1}.

Anal. Calcd. for $C_{13}H_{12}Cl_2N_4O_5$: C, 41.60; N, 14.93; H, 3.20. Found: C, 42.0; N, 14.7; H, 3.1.

(4-Chloro-2,6-dimethoxy-5-pyrimidinyl)-3,4,5-trimethoxyphenylmethane **9**.

A mixture of secondary alcohol **5e** (0.69 g, 1.86 mmoles), sodium borohydride (0.35 g, 9.2 mmoles), and anhydrous aluminium(III) chloride (0.7 g, 5.2 mmoles) in tetrahydrofuran (25 ml) was heated under reflux for 2 hours. The mixture was then cooled, 10 ml of water was added to give two clear phases and the whole mixture was extracted with ethyl acetate (4 x 50 ml). The extract was dried (calcium chloride) and evaporated under reduced pressure the crude product was purified by column chromatography on silica gel with a mixture of dichloromethane-ethyl acetate 9:1 as an eluent to give 375 mg (57%) of **9**, mp 103°; ^{1}H nmr (deuteriochloroform): δ 3.78 (s, 3H, OCH_3), 3.80 (s, 6H, OCH_3), 3.96 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 6.46 (s, 2H, phenyl) ppm; ir (potassium bromide): ν 2940, 2930, 1590, 1550 cm^{-1}.

Anal. Calcd. for $C_{16}H_{19}ClN_2O_5$: C, 54.16; N, 7.90; H, 5.36. Found: C, 53.9; N, 7.8; H, 5.1.

(2,4-Dimethoxy-5-pyrimidinyl)-3,4,5-trimethoxyphenylmethane **10**.

A solution of **9** (0.19 g, 0.53 mmole) in ethanol (15 ml) containing 20 mg of 10% palladium-on-carbon was hydrogenated at atmospheric pressure. Uptake of hydrogen was complete in 1 hour. The catalyst was removed by filtration and the filtrate evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel with a mixture of di-

chloromethane-ethyl acetate 1:1 as an eluent to give 56.6 mg (33%) of **10**, mp 77°; ^{1}H nmr (deuteriochloroform): δ 3.83 (m, 11H, 3OCH_3, CH_2), 3.98 (s, 3H, OCH_3), 4.00 (s, 3H, OCH_3), 6.43 (s, 2H, phenyl) ppm; ir (potassium bromide): ν 2940, 1610, 1595, 1510 cm^{-1}.

Anal. Calcd. for $C_{16}H_{20}N_2O_5$: C, 60.00; N, 8.75; H, 6.25. Found: C, 59.7; N, 8.7; H, 6.2.

(4-Chloro-2,6-dimethoxy-5-pyrimidinyl)methanol **11**.

A stirred solution of **5f** (1 g, 5 mmoles) in methanol (50 ml) was added sodium borohydride. After 30 minutes methanol was distilled under reduced pressure. The residue was extracted with dichloromethane (2 x 20 ml). The organic extract was dried (magnesium sulfate) and evaporated. The crude product was purified by column chromatography on silica gel with a mixture of dichloromethane-ethyl acetate 9:1 as an eluent to give 787 mg (77%) of **11**, mp 96°; ^{1}H nmr (deuteriochloroform): δ 2.30 (d, 1H, OH, J = 6 Hz), 3.98 (s, 3H, OCH_3), 4.03 (s, 3H, OCH_3), 4.70 (d, 2H, CH_2) ppm.

Anal. Calcd. for $C_7H_9ClN_2O_3$: C, 41.07; N, 13.69; H, 4.40. Found: C, 40.9; N, 13.5; H, 4.3.

(2,4-Dimethoxy-5-pyrimidinyl)methanol **12**.

A solution of **11** (0.78 g, 3.8 mmoles) in ethanol (15 ml) containing 0.2 g of 10% paladium on carbon was hydrogenated at atmospheric pressure. Uptake of hydrogen was complete in 1 hour. The catalyst was removed by filtration and the filtrate evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel with a mixture of dichloromethane-ethyl acetate 8:2 to give 161 mg (25%) of **12**, mp 123°; ^{1}H nmr (deuteriochloroform): δ 2.48 (s, 1H, OH), 4.00 (s, 3H, OCH_3), 4.05 (s, 3H, OCH_3), 4.58 (s, 2H, CH_2), 8.18 (s, 1H, H_6) ppm; ir (potassium bromide): ν 3200, 3020, 3000, 1610, 1500 cm^{-1}.

Anal. Calcd. for $C_7H_{10}N_2O_3$: C, 49.41; N, 16.45; H, 5.88. Found: C, 49.9; N, 16.1; H, 6.0.

4-Chloro-2,6-dimethoxy-5-*E*-(methoxycarbonylethenyl)pyrimidine **13**.

Palladium(II) diacetate (5 mg, 0.02 mmole) was added to a mixture of 4-chloro-2,6-dimethoxy-5-iodopyrimidine **5g** (0.5 g, 1.7 mmoles), methyl acrylate (0.39 ml, 4.25 mmoles), triethylamine (0.31 ml, 2.2 mmoles) in dry dimethylformamide (4 ml). The stirred mixture was heated for 24 hours. The precipitate of palladium(0) was removed by filtration and washed with ether. The solution was evaporated under reduced pressure and the crude product purified by column chromatography on silica gel with dichloromethane to give 88 mg (20%) of **13**, mp 138°; ^{1}H nmr (deuteriochloroform): δ 3.85 (s, 3H, OCH_3), 4.07 (s, 3H, OCH_3), 4.13 (s, 3H, OCH_3 ester), 7.50 (d, 1H, CH, J = 16 Hz), 7.83 (d, 1H, CH) ppm; ir (potassium bromide): ν 3000, 1710, 1630, 1500 cm^{-1}.

Anal. Calcd. for $C_{10}H_{11}ClN_2O_4$: C, 46.42; N, 10.83; H, 4.25. Found: C, 46.4; N, 10.7; H, 3.9.

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